Specific Heat, Charge Release and Dielectric Constant of PZT Ceramics

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Specific Heat, Charge Release and Dielectric Constant of PZT Ceramics

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Dielectric constant, specific heat and charge release measurements have been performed to study the F_{RL}-F_{RH} and F_{RH}-P_C phase transitions in Zr rich PZT ($PbZr_{1-x}Ti_xO_3$). Both transitions have been described together by means of a two order parameters effective field model, in order to include the effects of cation shifts (related to polarization) and the tilt of the oxygen octahedra. The behavior of the physical properties is shown to be described consistently.

I. INTRODUCTION

The dielectric properties, spontaneous polarization and specific heat measurements are widely used to study the ferroelectric phase transitions. A significant number of ferroelectric materials present more than one phase transition. The mixed system $PbZr_{1-x}Ti_xO_3$ is well known to present several phases [1], depending on Zr/Ti content, x. This material presents ferroelectric first order phase transitions [2] from the prototype cubic phase P_C (Pm3m) for x lower than about 0.26. Two ferroelectric rhombohedral phases appears separated by an isostructural phase transition. Michel *et al.* [3] determined, using an X-ray and neutron diffraction measurements, the space symmetry groups corresponding to these two phases, being R3c for the low-temperature phase (denoted F_{RL}) and R3m for the high-temperature phase (denoted F_{RH}). The main difference between this two phases consists in the tilt of the oxygen octahedra [4], which produces the doubling of the unit cell.

In this paper we present results of dielectric, pyroelectric and specific heat measurements of $PbZr_{1-x}Ti_xO_3$ (x=0.03, 0.04, 0.05) ceramics in the temperature range from 25 °C to 300 °C covering both: the ferroelectric (F_{RH}-P_C) and isostructural (F_{RL}-F_{RH}) phase transitions. The two order parameters generalized effective field model is used to describe and explain the observed anomalies of the specific heat behavior.

II. EXPERIMENTAL

The studies presented in this paper were performed on ceramic samples of the mixed system $PbZr_{1-x}Ti_xO_3$ with 1% by weight of Nb_2O_5, for three compositions: x=0.03, 0.04 and 0.05, prepared at the Shanghai Institute of Ceramics (SICCAS-China). The dielectric measurements have been done using an automatic Hewlett-Packard Bridge LCR Meter (4284A), with a heating rate of 20 °C/h. The specific heat measurements were made using a Perkin-Elmer DSC 7 Calorimeter, with a heating rate of 10 °C/min. The spontaneous polarization measurements were performed using a charge release device based in that due to Bernard *et al.* [5] which measures the pyroelectric charge released by the sample during the heating cycle [6] at a rate of 20 °C/h.

III. RESULTS

In order to characterize the two above mentioned phase transitions we have measured the dielectric constant (ϵ), the spontaneous polarization [6] (P_s) and the ferroelectric specific heat (ΔC_p) in the range 25 °C to 300 °C, covering, as mentioned before, the ferroelectric-paraelectric (F_{RH}-P_c) and the isostructural (F_{RL}-F_{RH}) phase transitions.

Figure 1 shows $P_s(T)$, $\epsilon(T)$ and $\Delta C_p(T)$ for x= 0.03 in the range 25 to 300 °C encompassing both phase transitions. The slight difference in phase transition temperatures as given by $P_s(T)$ and $\Delta C_p(T)$ has been taken care of by plotting the specific heat data, to be compared below with $(-\beta/2)\ dP_s^2/dT$, first at the F_{RH}-P_C transition, and then at the F_{RL}-F_{RH} transition, in the form ΔC_p vs. (T-T_{FP}), ΔC_P vs. (T-T_{LH}), respectively. It can be seen that both transitions are discontinuous (1st. order). The ferroelectric-paraelectric transition takes place at $T_{FP}\approx$ 243.0 °C, while the isostructural phase transition at 58.2 °C, for this composition.

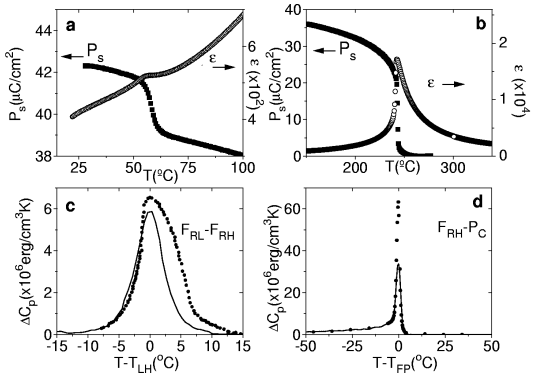

Fig. 1. PZT with x= 0.03. Spontaneous polarization (P_s), dielectric constant (ϵ), and specific heat in the range of temperature covering the F_{RL}-F_{RH} and F_{RH}-P_C phase transitions. (squares: spontaneous polarization, ∘ : dielectric constant, • : specific heat, — : specific heat calculated by Eq. (7) in (c), fitted by Eq. (5) in (d)). CGS units have been used for ΔC_p in order to make β parameter dimensionless (see text).

Figures 2 and 3 give the corresponding results for x= 0.04 and x= 0.05, respectively. Again both transitions are first order. The general behavior of the specific heat is similar in the three cases, but we may note that both transition temperatures first decrease from x= 0.03 to 0.04 and then increase from x= 0.04 to x= 0.05. The respective sequences of transition temperatures [6] are T_{LH}= 58.2, 42.9, 63.7 °C and T_{FP}= 243.0, 233.4, 246.3 °C, for increasing x.

It can be seen in Figs. 1-3 that, although the small anomaly in dielectric constant at T_{LH} makes difficult the observation of the F_{RL}-F_{RH} transition, the jump in the spontaneous polarization (about 3 μC/cm^2) is clearly visible in the pyroelectric charge release measurements [6].

In order to compare the observed behavior of the specific heat in the vicinity of the phase transitions we will first examine the ferroelectric-paraelectric transition to get an estimated value of the dipolar effective field

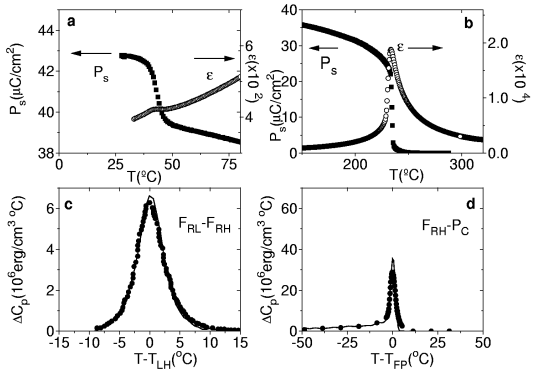

Fig. 2. PZT with x= 0.04. Spontaneous polarization (P_s), dielectric constant (ϵ), and specific heat (ΔC_p), observed and calculated. Symbols are the same as in Fig. 1.

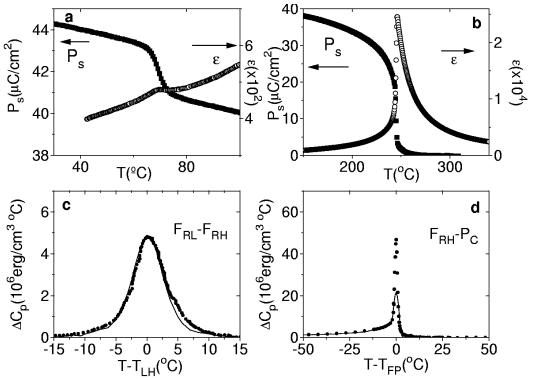

Fig. 3. PZT with x= 0.05. Spontaneous polarization (P_s), dielectric constant (ϵ), and specific heat (ΔC_p), observed and calculated. Symbols are the same as in Fig. 1.

coefficient β=E_s/P_s, which can be independently obtained by means of $\beta = k_B T_C/N\mu^2$ where k_B is Boltzmann's constant, T_C is the extrapolated Curie temperature ($T_C \leq T_{FP}$), N= $1/a^3 \approx 1.56\times10^{22}$ dipoles/cm^3 and $\mu = P_{so}$/N, the elementary dipole moment in cgs-esu units. Then we will use the β values obtained from the ferroelectric-paraelectric transition to fit the specific heat peak at the isostructural F_{RL}-F_{RH} transition. To this end we first will review briefly the two order parameters model [7–9] describing the tilt-polarization coupling in Zr-rich PZT, from which we will get ΔC_p as a function of P_s(T). The calculated behavior of ΔC_p as a function of T-T_{LH} obtained in this way is plotted in Figs. 1-3 along with the experimental data.

IV. TWO ORDER PARAMETERS MODEL

A two order parameters effective field theory has been fruitfully used [2] previously to describe the ferroelectric behavior of Zr-rich PZT. This theory allowed us to describe the dielectric constant and the spontaneous polarization and will be used here to describe the specific heat in terms of the basic effective field parameters for different compositions of PZT ceramic samples. In this theory, the polarization, P, is expressed as a function of the temperature in the following way:

$$\frac{P}{N\mu} = \tanh\left(\frac{E_{\text{eff}}\mu}{k_B T}\right) \tag{1}$$

where [2] $E_{\text{eff}} = E + \beta P + \gamma P^3 + \delta P^5 + \ldots$ is the effective field, μ is the elemental dipole in the lattice and N is the number of dipoles per unit volume. Then $P_s(0)$= P_{so}=$N\mu$ is the saturation value of the spontaneous polarization, $P_s = P(E = 0)$.

The coupling between the oxygen octahedra tilt and the cation displacements in the F_{RL} phase is the main factor responsible for the increment of the spontaneous polarization with the respect to that of the zero-tilt F_{RH}

phase. Previous works included the tilt angle as an additional order parameter in a phenomenological Landau's theory [7]. In our case, we describe the influence of the tilt order parameter within the framework of a microscopic statistical theory.

We assume, that for the tilt order parameter it is possible to write an equation of state similar to Eq. (1), as given in Ref. [9]

$$\frac{\theta}{N' \mid 2\omega \mid} = \tanh\left(\frac{\mid X_{\rm eff} \mid\mid 2\omega \mid}{k_B T}\right), \qquad (2)$$

where θ is the macroscopic tilt angle of the oxygen octahedra, N is the number of doubled unit cells per unit volume, being $|2\omega|$ the microscopic tilt per unit cell. $\theta_{\rm so}$=$N'|2\omega|$ is the saturation value of the macroscopic tilt angle, and $|X_{\rm eff}|$ is the associated staggered torsional effective field, which can be expressed as $|X_{\rm eff}| = X+\beta_{\rm t}\theta_{\rm s}+\gamma_{\rm t}\theta_{\rm s}^3+\delta_{\rm t}\theta_{\rm s}^5+\ldots$. Because there is no external torsional field (X=0), the tilt is spontaneous ($\theta = \theta_{\rm s}$).

The tilt of the oxygen octahedra and the polarization are allowed to couple. Similar arguments [9] to that used in Eqs. (1) and (2) give now for the total polarization:

$$\frac{P}{N_\mu} = \frac{P_s}{N_\mu} + \frac{\Delta P_s}{N_\mu} = \tanh\left[\frac{W_d}{k_B T} + \frac{W_t}{k_B T}\right], \qquad (3)$$

where $W_{\rm d} = \mu E_{\rm eff}$ is the interaction energy between the internal field and elemental dipole moment, and $W_{\rm t}$=$|2\omega||X_{\rm eff}|$ is the interaction energy between the staggered torsional field and the elemental torsion of the oxygen octahedra. The change in the spontaneous polarization at T<$\rm T_{LH}$ is caused by the tilt ($\theta_{\rm s} \neq 0$) and is expressed as [9]

$$\Delta P_s = \frac{(P_{so}^2 - P_s^2)\theta_s}{(P_{so}\theta_{so} + P_s\theta_s)}. \qquad (4)$$

The ferroelectric contribution to the specific heat in the absence of tilt can be written [10], taking into account that we will use the observed $P_{\rm s}(T)$ data, as

$$\Delta C_p = -\frac{1}{2}\frac{d(E_s P_s)}{dT} \approx -\frac{1}{2}\beta\frac{dP_s^2}{dT} \quad (T \approx T_{\rm FP}) \qquad (5)$$

where the relation $E_{\rm eff}$≈$\beta P_{\rm s}$ has been used and β, as used before, can be estimated as β= $\rm k_B T_C/N^2$≈ 0.07, which comes close to β determined from $\Delta \rm C_p$ at $\rm T_{FP}$, for x= 0.03, 0.04 and 0.05.

To include the effect of the $\rm O_6$ tilt at temperatures below the $\rm F_{RL}$-$\rm F_{RH}$ transition, we express the specific heat as,

$$\Delta C_p = -\frac{1}{2}\beta\frac{d(P_s + \Delta P_s)^2}{dT} - \frac{1}{2}\beta_t\frac{d\theta_s^2}{dT} \quad (T \approx T_{\rm LH}). \qquad (6)$$

Equations (5) and (6) reproduces well the behavior of the ferroelectric specific heat at both transitions.

V. DISCUSSION

The magnitude of the second term ($\beta_{\rm t} \rm d\theta_s^2/dT$) in Eq. (6) was found to be much smaller than that of the main term involving ($\rm P_s \Delta P_s$). The part corresponding to $\rm dP_s{}^2/dT$ forms part of the background. Then

$$\Delta C_p \approx -\beta\frac{d}{dT}(P_s \Delta P_s) \quad (T \approx T_{\rm LH}). \qquad (7)$$

The β values obtained for best fits of $\Delta \rm C_p$ (T≈ $\rm T_{FP}$) are β= 0.076, 0.060 and 0.060, for x= 0.03, 0.04 and 0.05, respectively. Figs. 1-3 show the calculated peaks for $\Delta \rm C_p$ which fit nicely the observed $\Delta \rm C_p$ peaks measured by a DSC calorimeter.

The ferroelectric contribution to the specific heat at both transitions, therefore, was obtained using a single mean field parameter, β, and the spontaneous polarization vs. temperature data, by means of Eq. (5) and $\rm T_{FP}$ and Eq. (7) at $\rm T_{LH}$.

We can conclude that the temperature dependence of the spontaneous polarization at $\rm T_{FP}$ and at $\rm T_{LH}$, including the extra $\Delta \rm P_s$ coupled to the tilt, determines very well the behaviour of the specific heat at both transitions of PZT.

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